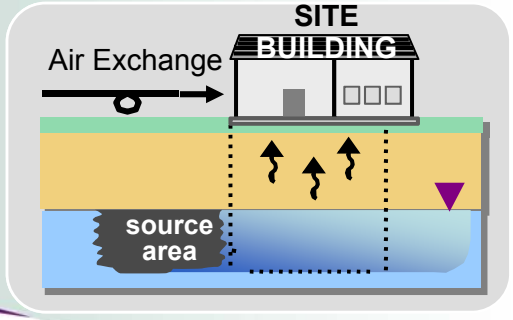

Field Methods to Distinguish Between Vapor Intrusion and Indoor Sources of VOCs

Thomas E. McHugh, PhD., D.A.B.T.
Kyle Gorder, M.S
Erik Dettenmaier, PhD

ESTCP

2012 DoD EMDQ Workshop

GSI ENVIRONMENTAL

75th AIR BASE WING

Report Documentation Page

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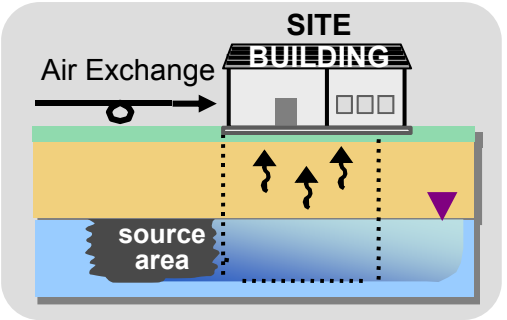
Vapor Intrusion: Field Methods

- Significance of Background VOC Sources
- Stable Isotope Analysis
- On-Site GC/MS Analysis



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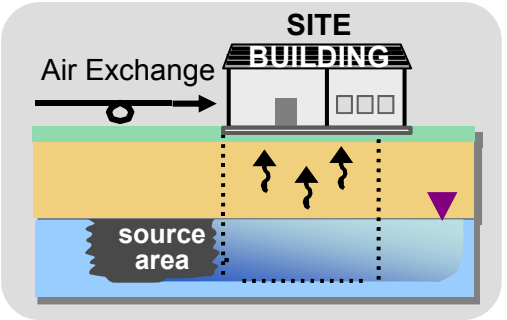

Source of Background Indoor Air Impacts

Key Sources of VOCs in Indoor Air:

- Ambient air
- Vehicles, gasoline
- Paints, adhesives
- Cleaning agents
- Insecticides
- Tobacco smoke
- Cosmetics, etc.

REFERENCES:

- USEPA, 1991, "Building Air Quality Guide"
- OSHA, 1999, "Tech Manual for Indoor Air Inv."

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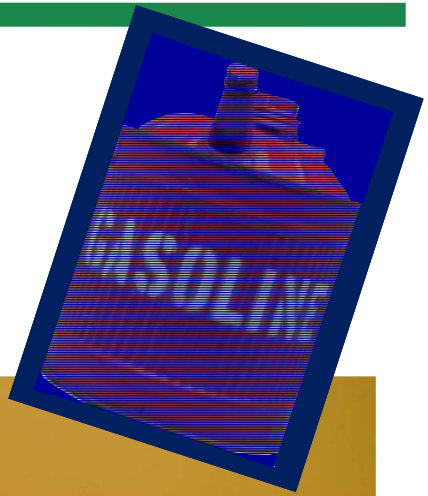

Background Sources of Indoor Air Impacts

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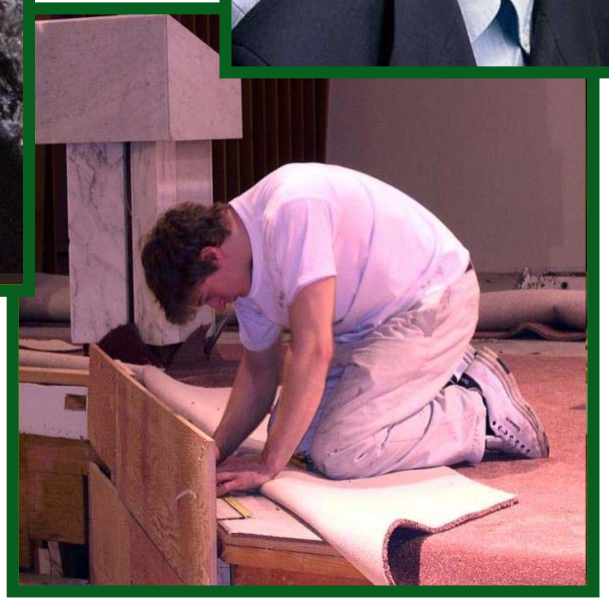


But We Don't Use "TOXIC" Chemicals Anymore

Email bulletin from vendor, October 2010:

Technical Update

Topics, trends, and news in the environmental industry…

TCE Contamination Affects Community's Water We

" The TCE, *which was banned from public use in the 1970s*, was detected at levels greater than the U.S. EPA's maximum contaminant level for public drinking water."

KEY POINT:

Many people believe that TCE and other chlorinated solvents are no longer used in industrial operations or consumer products.

Examples of Indoor Sources: *CVOCs*

Gun Cleaner: $19.95
>90% TCE

Pepper Spray: $3.99
>90% TCE

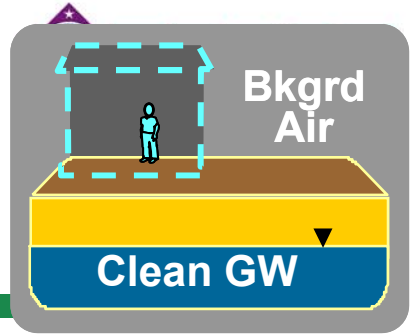
Hobby Glue: $4.95
>90% PCE

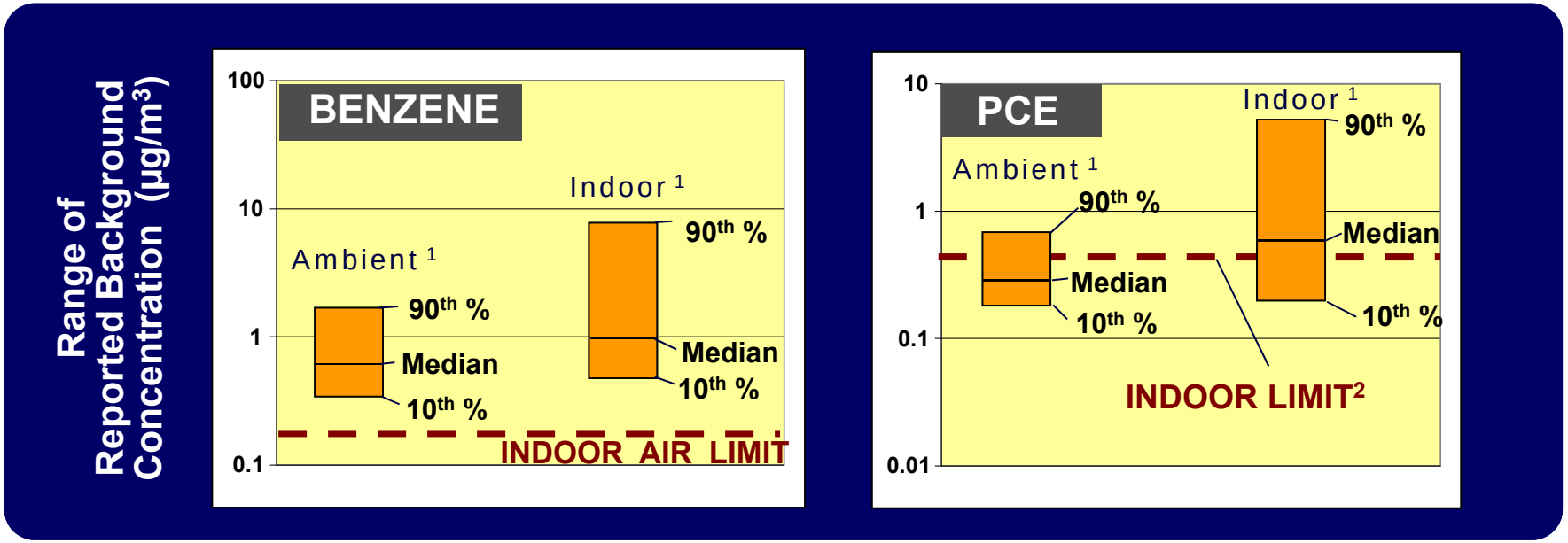
Plastic Ornament: $4.95
1,2-DCA

KEY POINT: **Chlorinated VOCs are legal and are still used in a wide variety of consumer products currently available for purchase.**

Significance of Background Sources

Importance of Background VOCs





KEY POINT: **Background sources of VOCs are ubiquitous in indoor and ambient air, commonly at concentrations exceeding risk-based limits for indoor air.**

1) Background concentrations from Sexton et al. 2004 ES&T 38(2); 423-430.
2) Indoor air limits from USEPA Master Screening Values Table, September 2008

Vapor Intrusion Investigations: *Advanced Methods*

GOAL

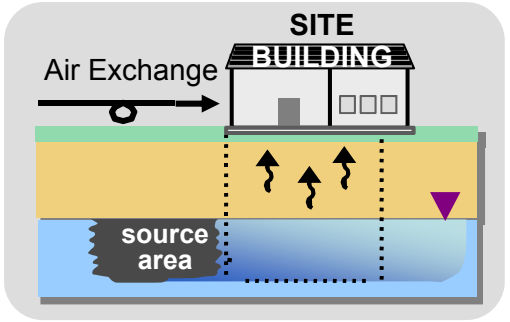
- **Identify source of indoor air VOCs quickly and economically, without need for multiple sampling episodes.**

METHODS

- ***Isotopic Analyses*** **to distinguish among various sources of VOCs**
- ***On-Site Vapor Analyses*** **using portable GC-MS**
- ***Building Pressure Control*** **ensure that VI is "turned on"**

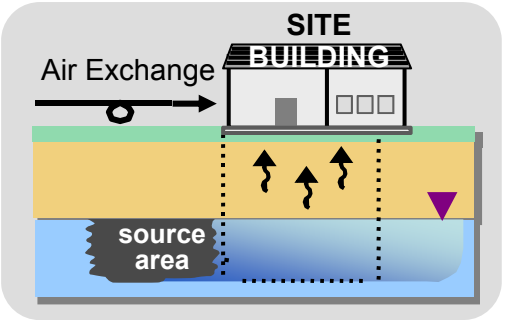
Vapor Intrusion: Field Methods

- Significance of Background VOC Sources
- ***Stable Isotope Analysis***
- On-Site GC/MS Analysis



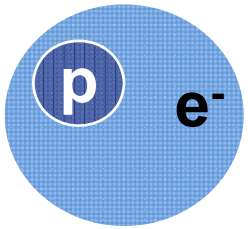
Vapor Intrusion: Field Methods

- **Significance of Background Sources**
- ***Stable Isotope Analysis***
  - ***Application to Vapor Intrusion***
    - ***Method Validation***
    - ***Field Application***
- **On-Site GC/MS Analysis**

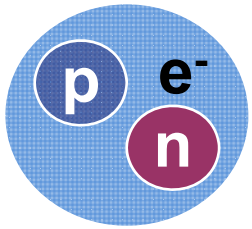


TECHNOLOGY DESCRIPTION

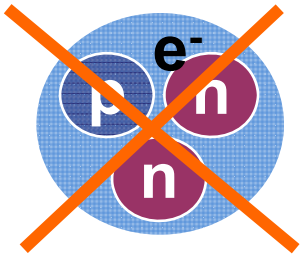
What are Stable Isotopes?



Hydrogen,
^{1}H



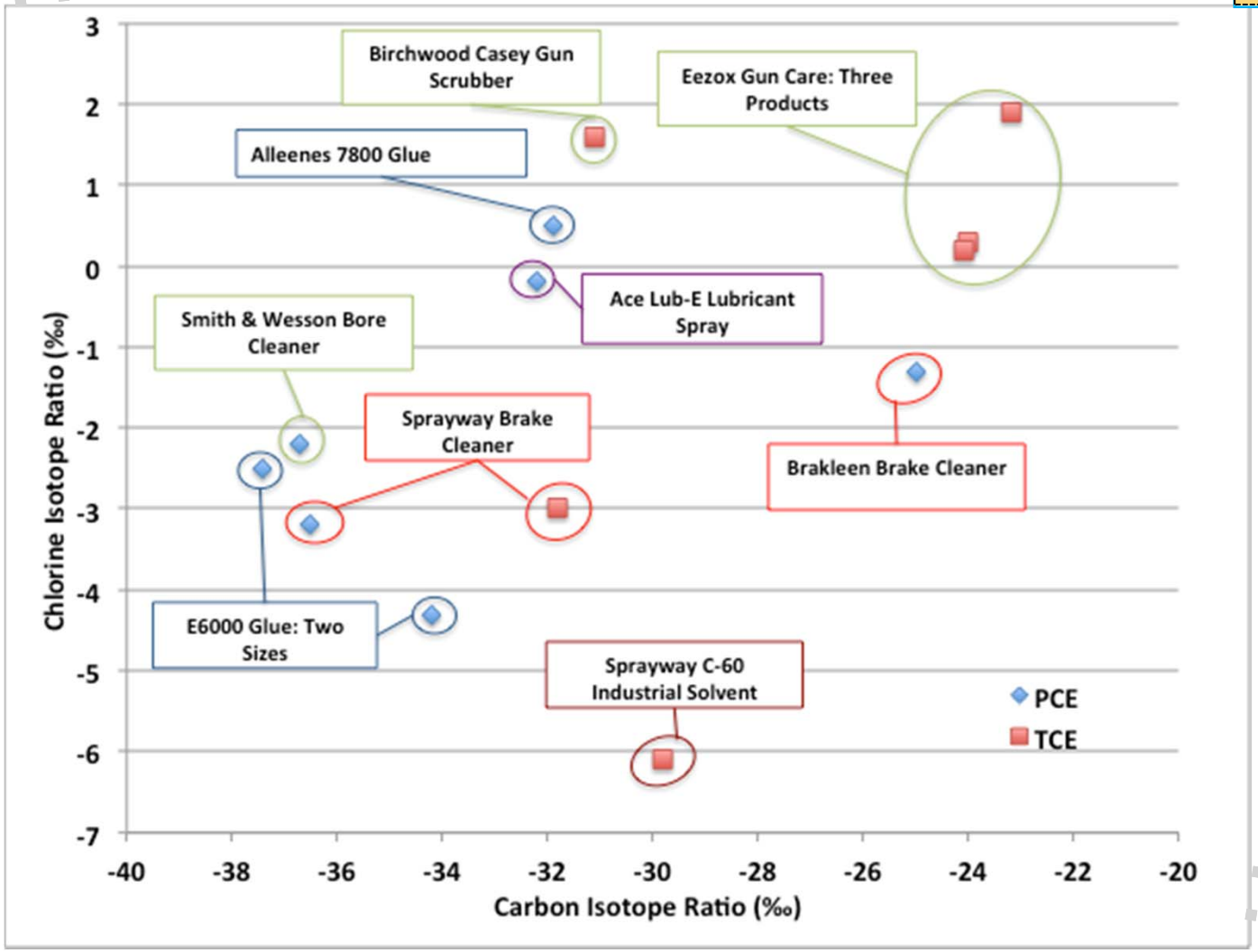
Deuterium,
^{2}H, D

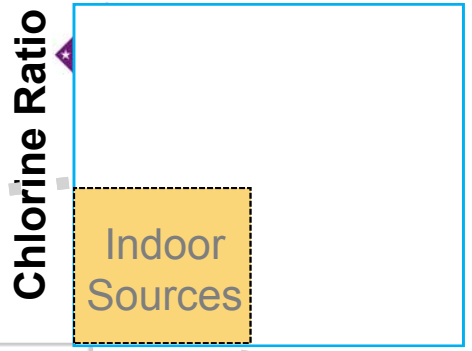


Tritium,
^{3}H, T

- Isotopes have the same number of protons – identical atomic number
- Isotopes have different number of neutrons – different atomic mass
- Stable isotopes do not undergo radioactive decay – tritium is not a stable isotope

ISOTOPE RATIOS: *INDOOR SOURCES*

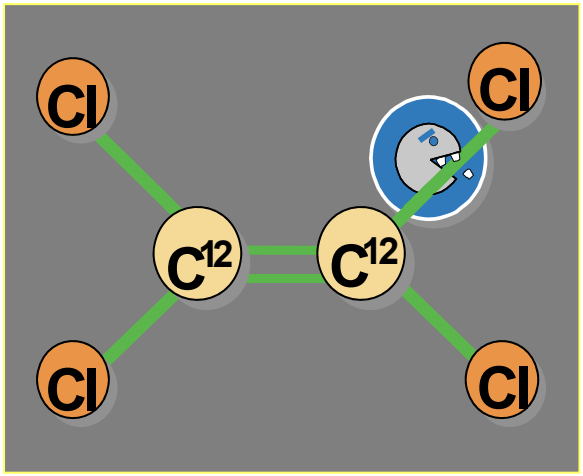


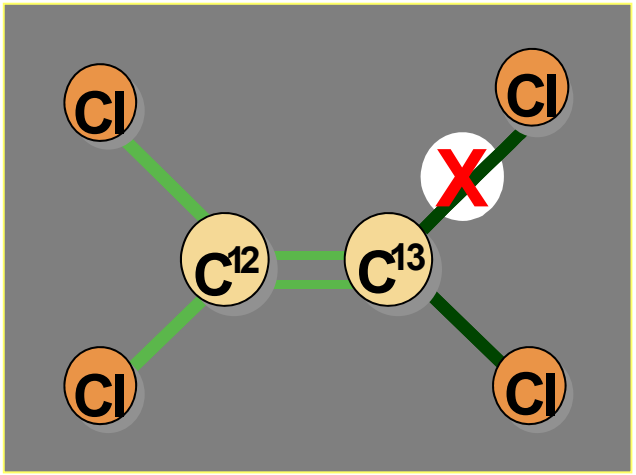


CHANGES IN THE SUBSURFACE

Stable Isotope Fractionation

Kinetic Effect: Biodegradation causes enrichment in PCE containing 13C



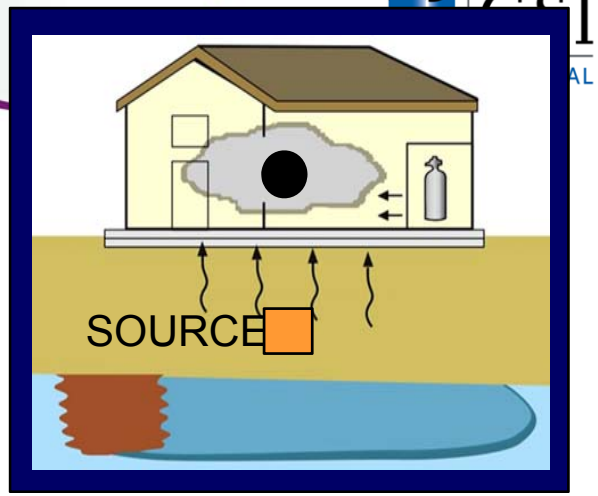


Biodegradation of PCE:

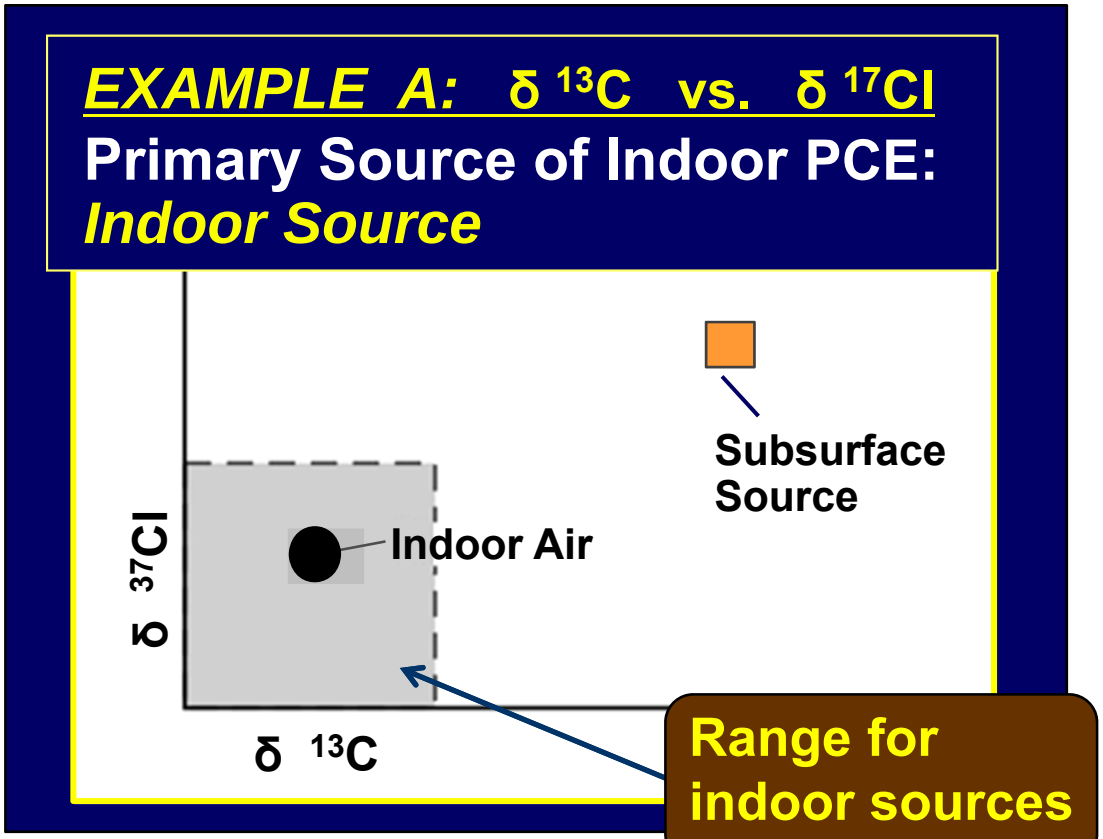
^{12}C – Cl bond easier to break than ^{13}C – Cl bond.

Key Point: ***Differences in isotope ratios between samples can indicate different sources: indoor vs. subsurface.***

Compound-Specific Stable Isotope Analysis, (C, Cl)



- CSIA: "Fingerprinting" method to distinguish between vapor intrusion and indoor sources
- Applicable to sites where biodegradation of subsurface VOCs has occurred, causing an isotope shift for subsurface source vs. indoor source.



CSIA = Compound-Specific Stale Isotope Analysis

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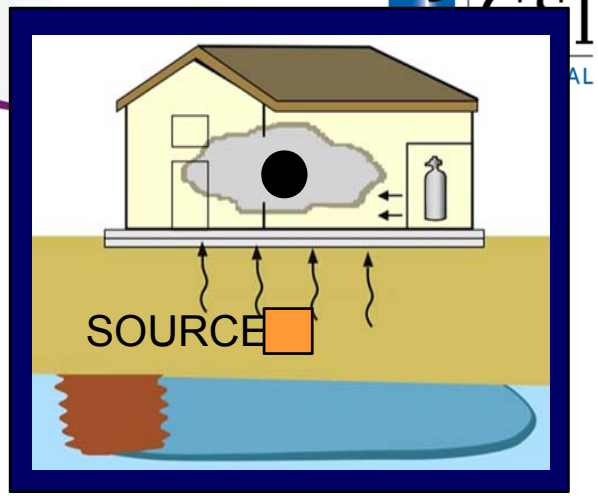

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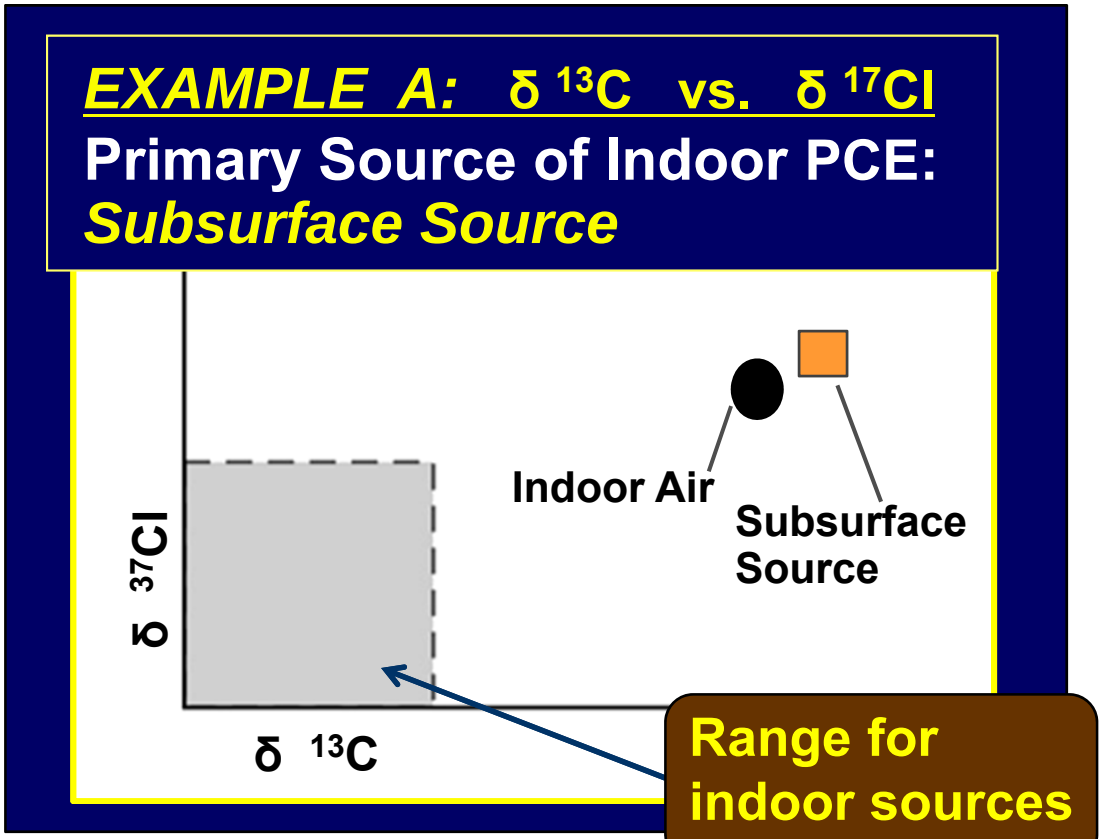
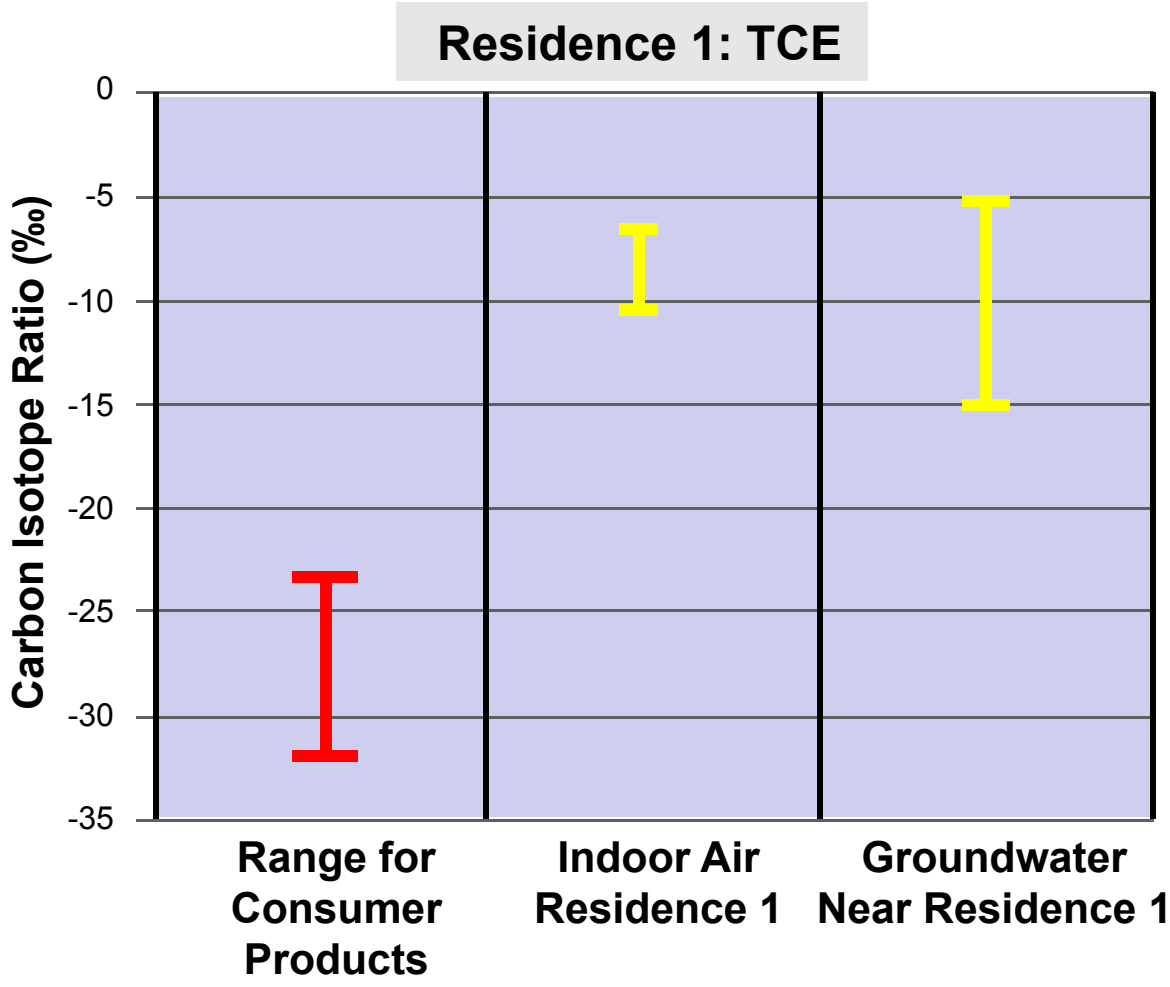


CSIA = Compound-Specific Stale Isotope Analysis

CSIA Example Results: *Indoor Air vs. Subsurface Vapor C^{12} / C^{13} Ratios*



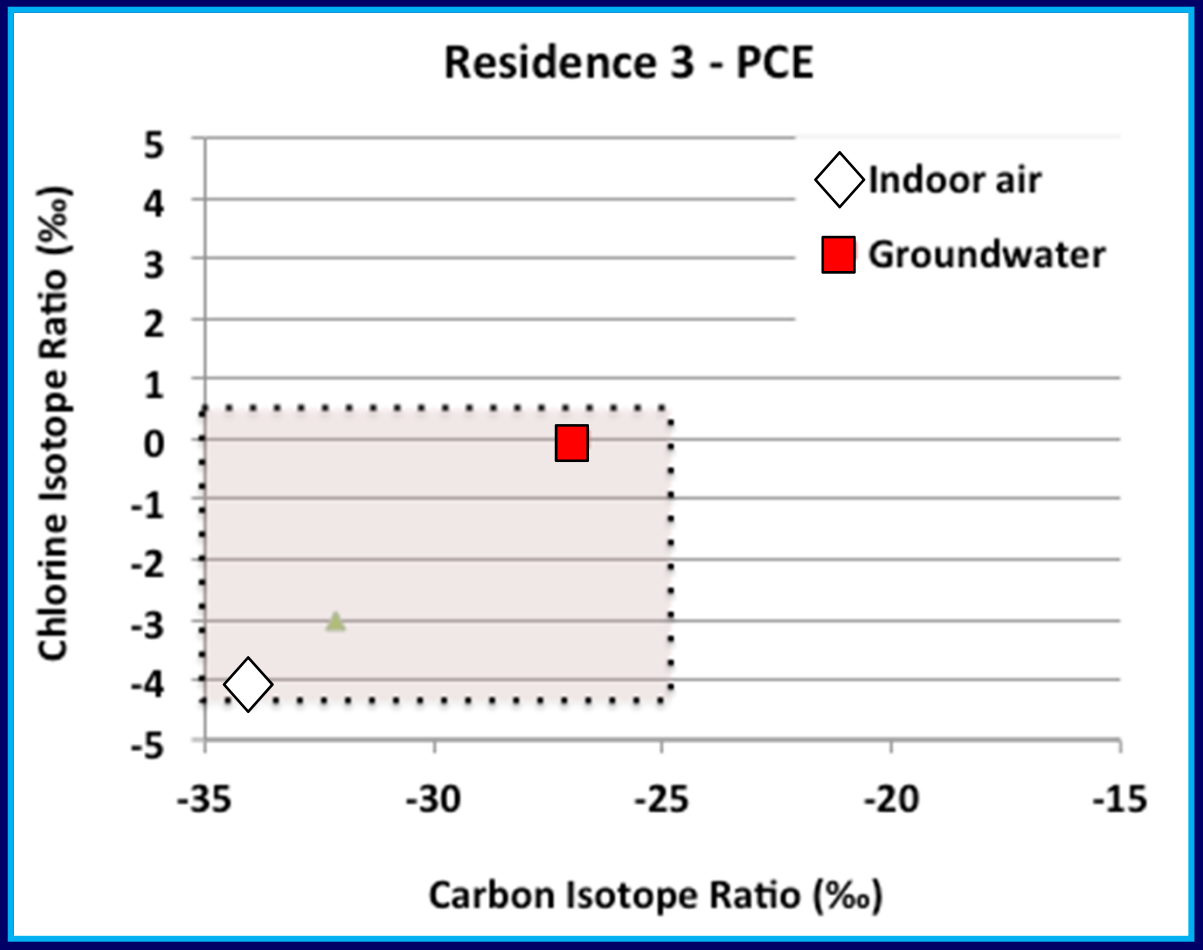
KEY FINDINGS:

- **TCE in indoor air matches TCE in groundwater**
- **TCE is too heavy to be an indoor source**
- **Vapor intrusion is occurring**

max

min

CSIA Example Results:
C^{12} / C^{13} and Cl^{35} / Cl^{37} Ratios



FINDING:

PCE in indoor air is from indoor source.

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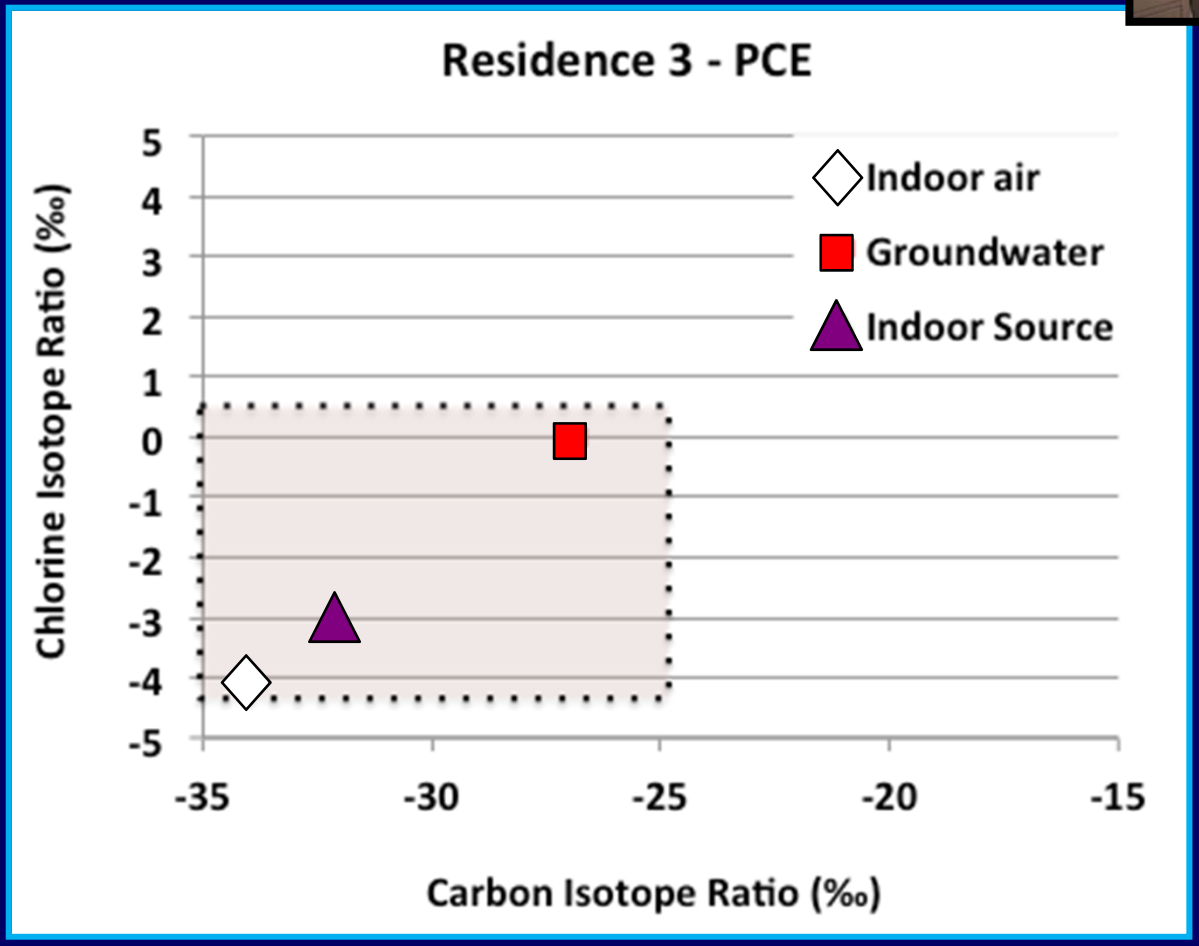

FINDING:

PCE in indoor air is from indoor source.

(E6000 glue.)

Vapor Intrusion: Field Methods

- **Significance of Background Sources**
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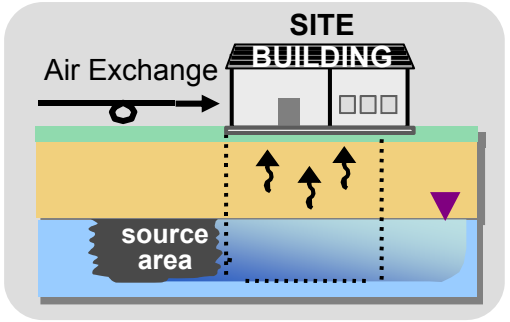
  - ***Method Validation***
  - ***Field Application***
- **On-Site GC/MS Analysis**



METHOD VALIDATION:
SORBENT TUBE SAMPLERS

Adsorbent Tubes

Air Sampling Pump

Results from Laboratory Validation Study

- **Sorbent**: Fractionation free performance from Carboxen 1016
- **Sampling Conditions**: Validated for wide range of humidity, sample volume, sample mass, and non-target VOC mass
- **Target VOCs**: Validated for PCE, TCE, and benzene

Report on Laboratory Method Validation:

Kuder et al., 2012 (To be posted at http://www.serdp-estcp.org/)

METHOD VALIDATION:

APPLICATION TO VAPOR INTRUSION

Site	■ Five residences over chlorinated solvent plume with TCE or PCE detected in indoor air ■ Near Hill AFB, Utah
Sampling Program	■ One indoor air sample from each residence ■ One to four groundwater or soil gas samples from near-by sample points
Results	■ Confirmed Vapor Intrusion: Two residences ■ Confirmed Indoor Sources: Two residences ■ Not Conclusive: One residences

Paper on Application of CSIA to Vapor Intrusion:

McHugh et al., 2011 Env. Sci. Technol. Vol. 45(14) pp. 5952-5958.

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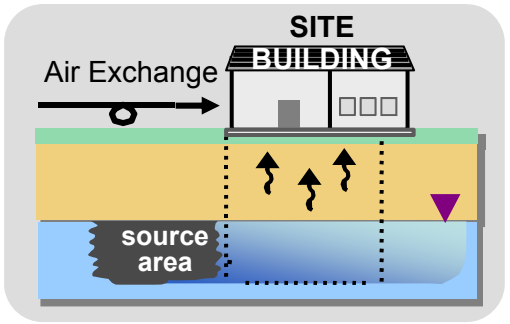


CSIA FOR VI: *FIELD APPLICATION*

Step 1A: **Characterize Isotope Ratios for Subsurface Source.**

Groundwater

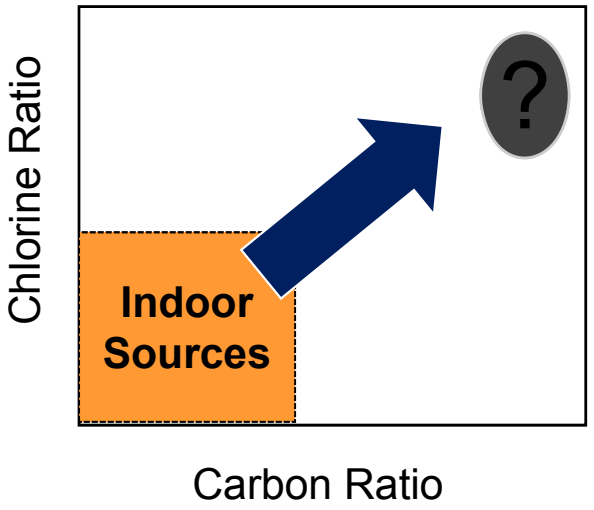
OR

Soil Gas

Conduct CSIA on groundwater sample from existing monitoring well

Conduct CSIA on soil gas sample

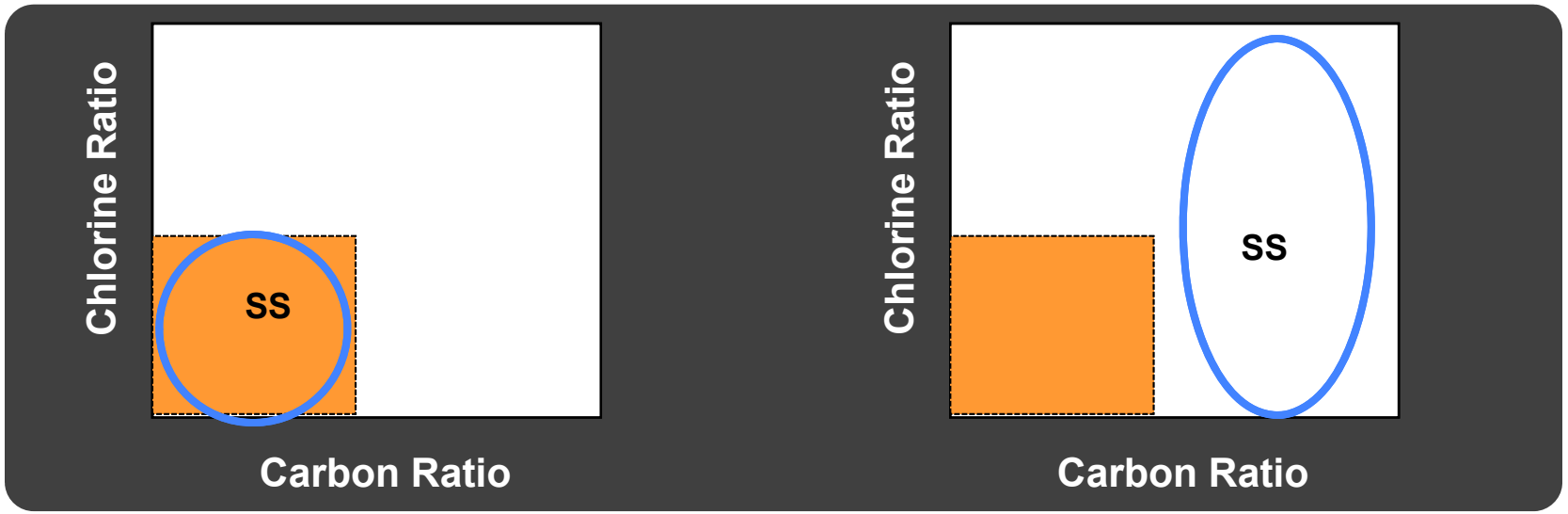
- **<100 ug/m^3 = sorbent tube**
- **100 to 500 ug/m^3 = 6L Summa**
- **> 500 ug/m^3 = 1L Summa**



KEY POINT: Can collect subsurface sample from existing sample point.

CSIA FOR VI: FIELD APPLICATION

Step 1B **Compare Isotope Ratios for Subsurface Source to Measured Range for Indoor Sources**



Subsurface source NOT enriched in heavy isotopes: *CSIA not likely to distinguish between indoor and subsurface sources.*

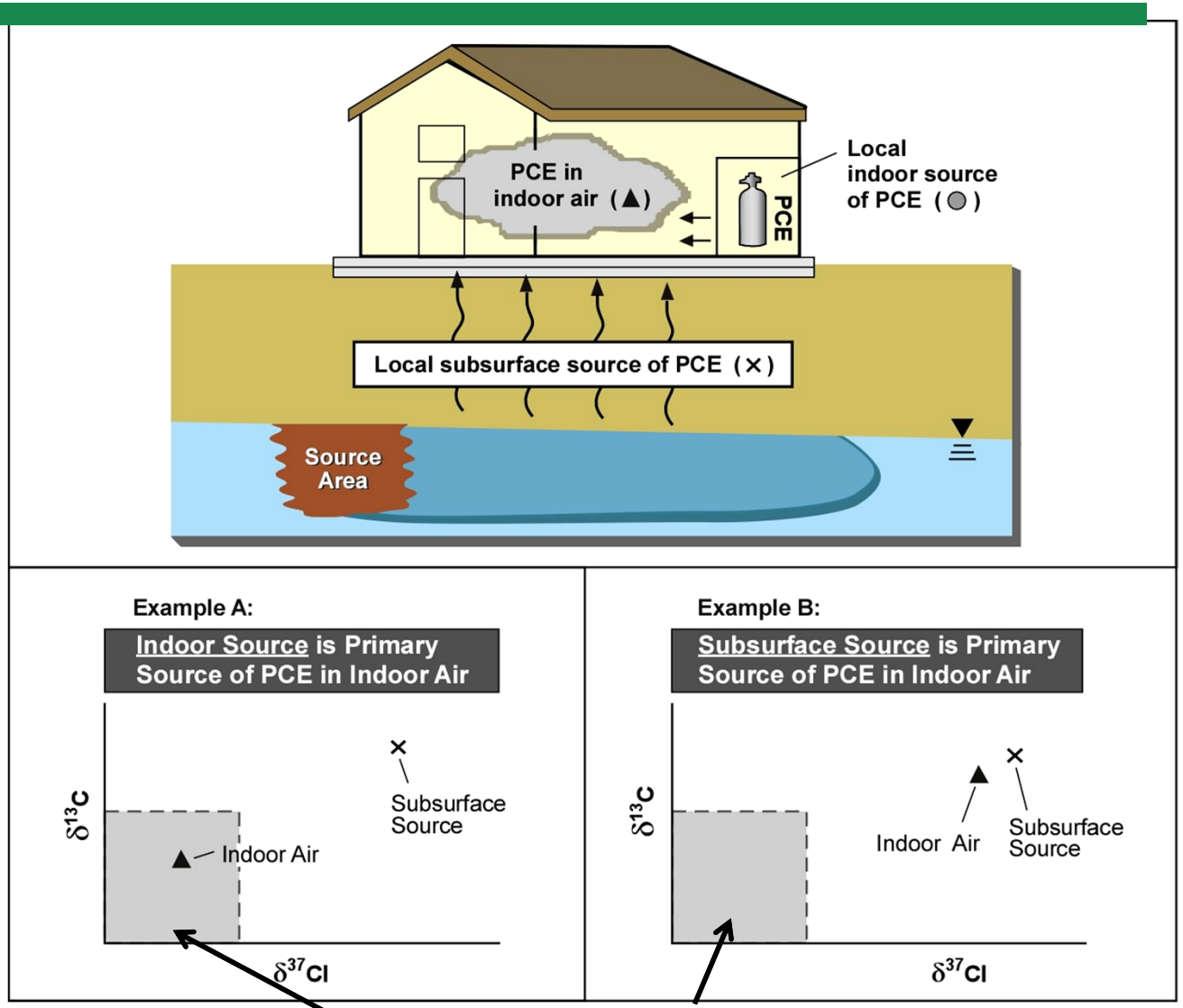
Subsurface source IS enriched in heavy isotopes: *CSIA applicable to vapor intrusion.*

CSIA FOR VI: FIELD APPLICATION

Step 2:

Collect indoor air samples for CSIA.

Compare results to indoor source range and site-specific subsurface source.



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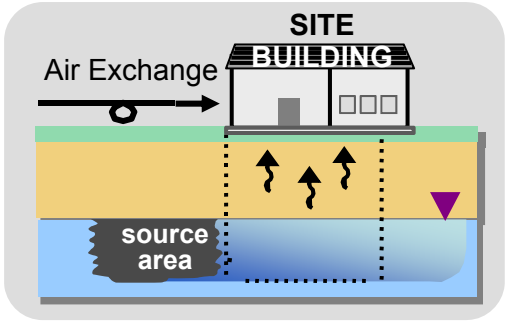
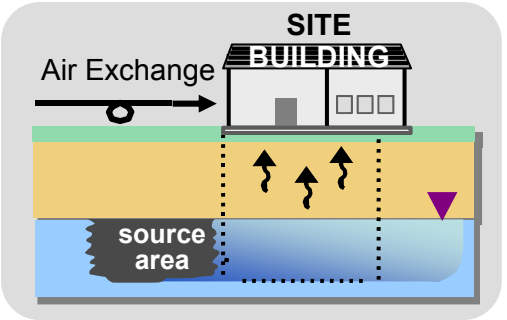


Vapor Intrusion: Field Methods

- **Significance of Background Sources**
- **Stable Isotope Analysis**
- ***On-Site GC/MS Analysis***
  - ***Overview***
  - ***Investigation Protocol***
  - ***Data Quality Considerations***



On-Site Vapor Analysis

What?

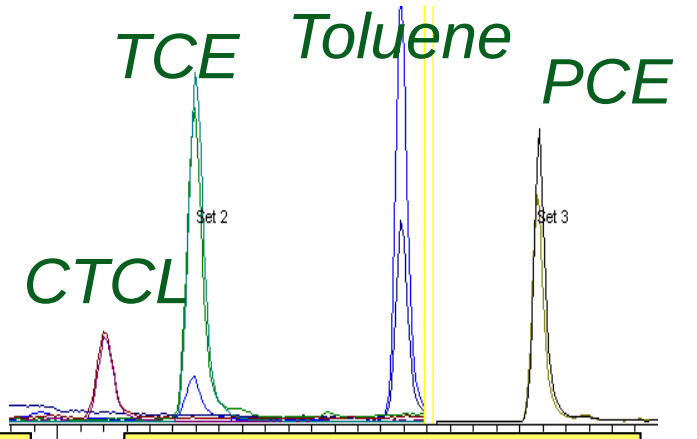
- On-site analysis (with low detection limits)
- Initial results guide collection of additional samples

When?

- Rapid identification of source(s) of VOCs in indoor air:
  - Time/building access is limited
  - Building with complex indoor sources
  - High concern from building occupants
  - Prior analyses are not definitive

On-Site Analysis

HAPSITE Instrument



Results in Field

On-Site Vapor Analysis Options

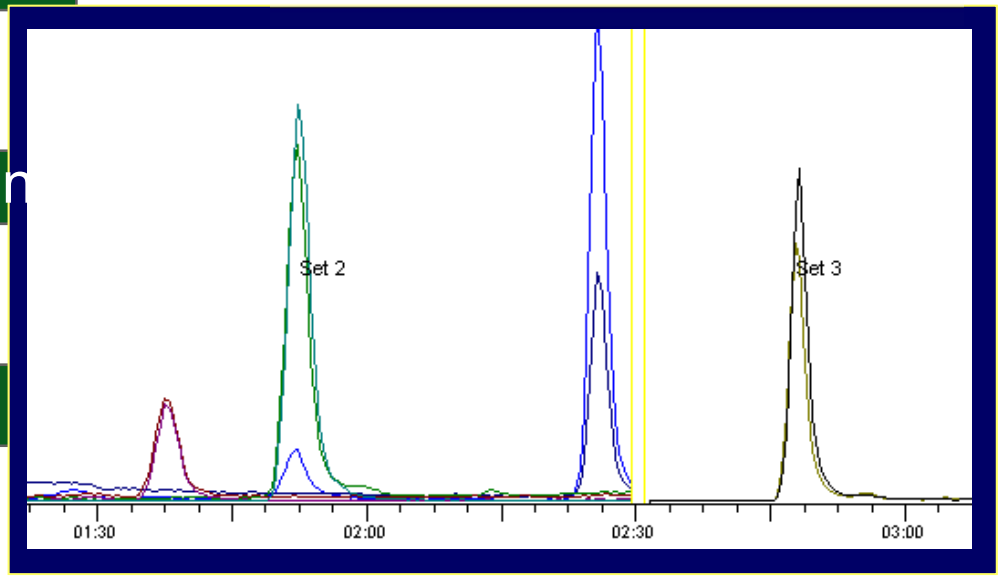
Option	Performance
HAPSITE Portable GC/MS ($3-5K/day)	▪ 0.2 ppbv detection limit for grab samples ▪ Less sensitive in survey model (i.e., continuous reading)
Mobile Lab GC/MS (>$5K/day)	▪ 1 to 10 ppbv detection limit for grab samples ▪ Need alternate instrument for survey

HAPSITE ADVANTAGES:

- Does both survey and analytical modes
- Compound-specific real-time survey
- Portable w/ on-site data management
- Less expensive than mobile lab

Instrumentation

- ***Inficon HAPSITE® GC/MS***
- ***Key features:***
  - Custom Methods
    - (~6 min) sample turn time
  - "Clean" chromatograms
    - Target VOCs in SIM mode
  - "Positive" identification
    - Full scan using NIST library
  - Low quantitation limits
    - Chlorinated aliphatics in ppt



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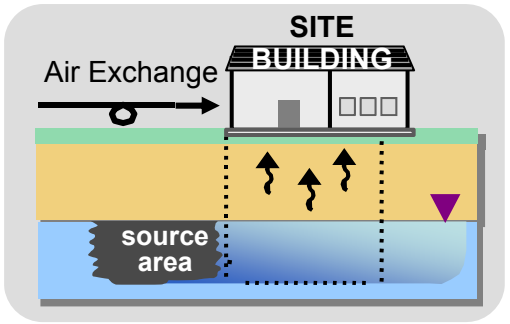
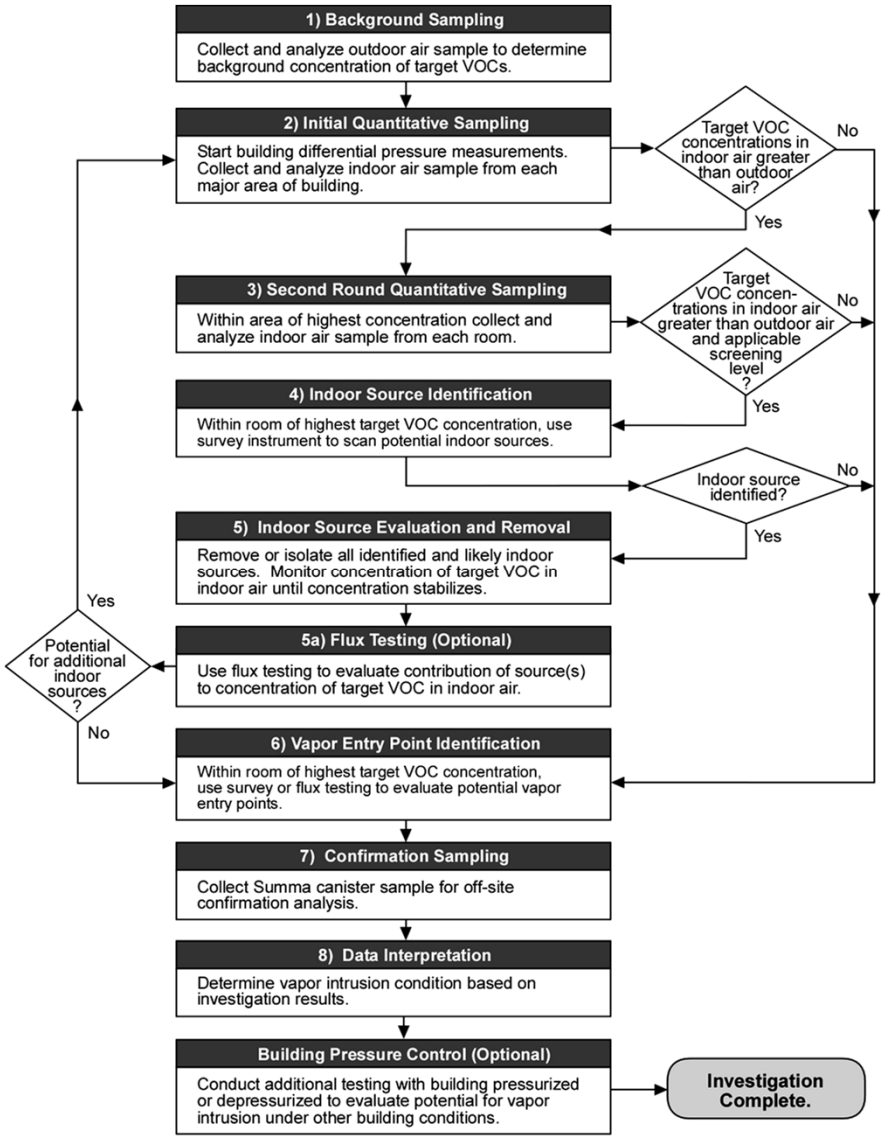


ON-SITE ANALYSIS FOR VI

INVESTIGATION PROTOCOL

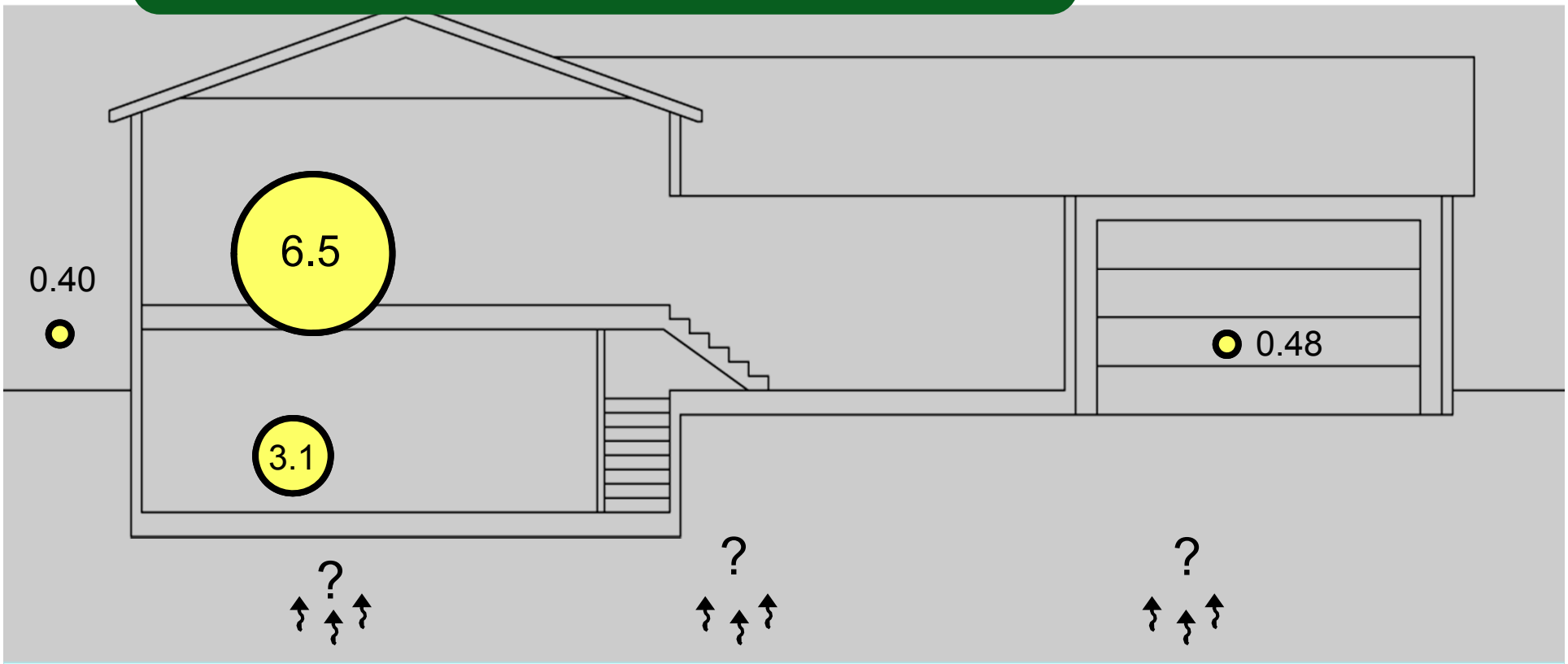
- Project planning
- Instrument operation, calibration, QA/QC
- Building operating conditions
- Step-by-step sampling program (see flow chart)
- Data interpretation



KEY POINT: **Comprehensive written protocol for application of on-site analysis approach.**

Investigation Protocol

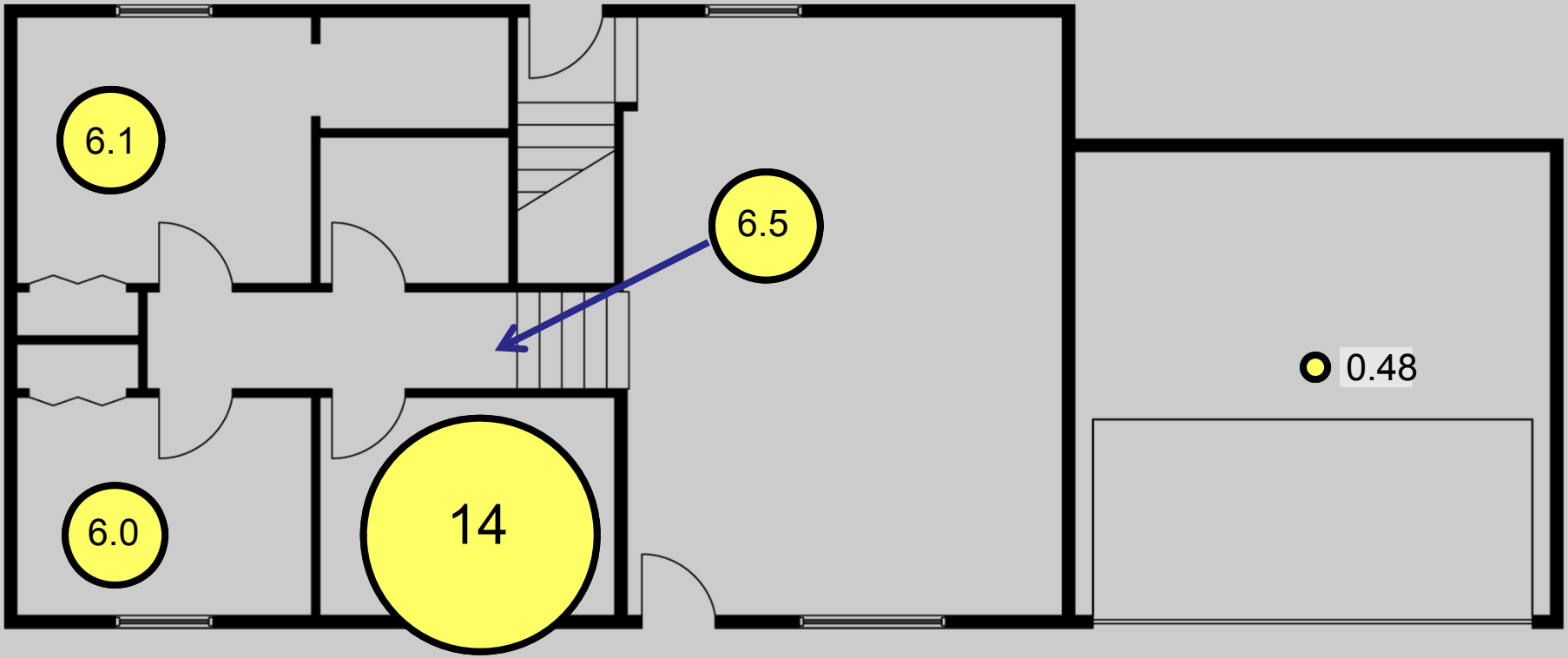
1) Outdoor Air (Background)
2) Area by Area Sampling



Dissolved PCE in Shallow Groundwater

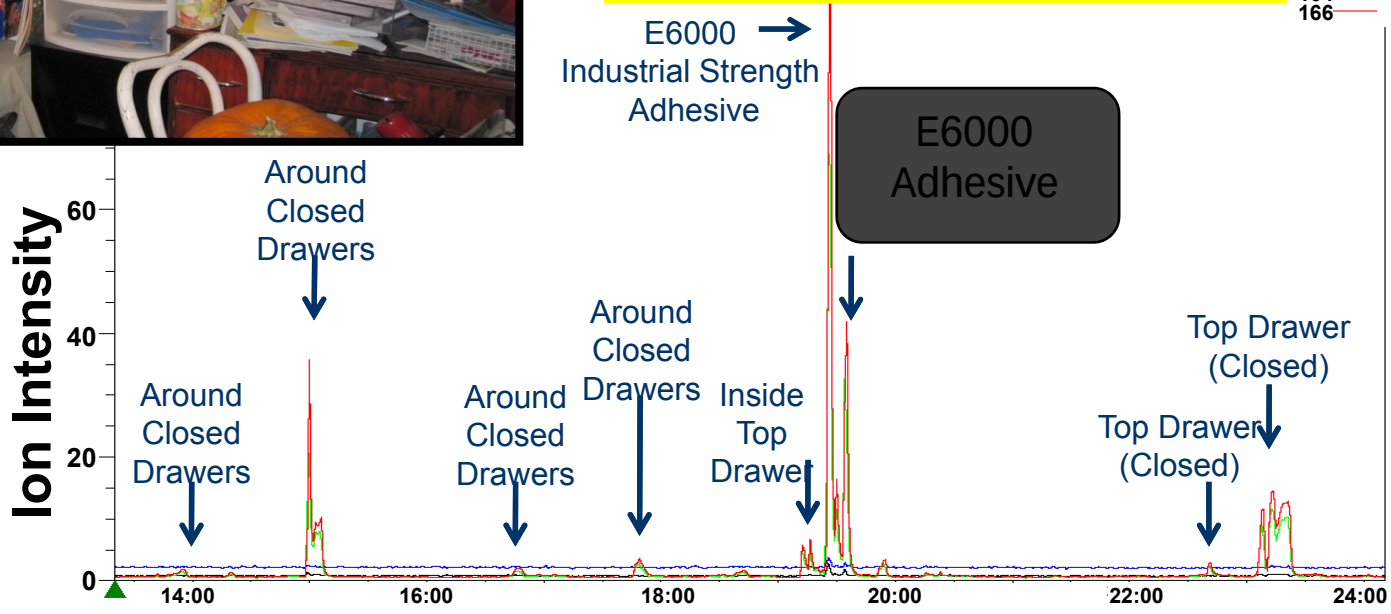
Investigation Protocol

3) Room by Room Sampling



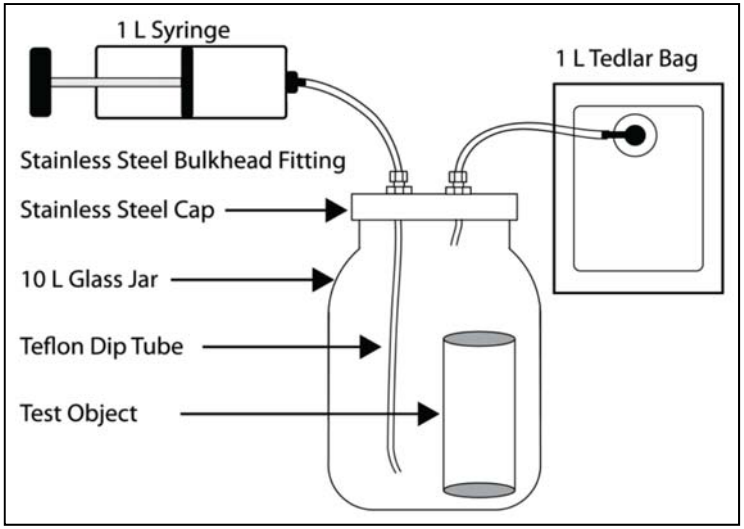
Investigation Protocol

4) Interior Source Identification



Investigation Protocol

5) Interior Source Evaluation and Removal



KEY QUESTION: **Is emission rate from identified source sufficient to account for VOC concentration in indoor air.**

Investigation Protocol

6) Vapor Entry Point Identification

Investigation Protocol

7) Confirmation Sampling

KEY POINT: **Samples for off-site analysis collected only after indoor sources have been identified and removed.**

Investigation Protocol

8) Data Interpretation

Table 3.5.2: Interpretation of On-Site Analysis Investigation Results - Baseline Sampling

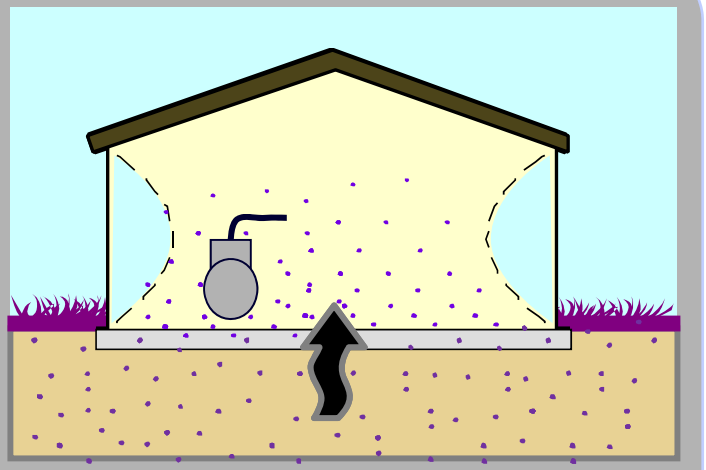
Concentration of Target VOC in Indoor Air	One or more indoor sources of target VOC identified but left in place[1]?	Vapor entry point(s) identified for target VOC?	Finding
Below screening level	No	No	No evidence of current vapor intrusion.
Below screening level	Yes	No	No evidence of current vapor intrusion.
Below screening level	No	Yes	No evidence of unacceptable current vapor intrusion. Evaluation of temporal variability may be warranted.
Below screening level	Yes	Yes	No evidence of unacceptable current vapor intrusion. Evaluation of temporal variability may be warranted.
Above screening level	No	No	Investigation results inconclusive
Above screening level	Yes	No	No evidence of current vapor intrusion
Above screening level	No	Yes	Current vapor intrusion occurring
Above screening level	Yes	Yes	Evidence of potential vapor intrusion, but contribution of vapor intrusion to indoor air impact not determined.

Optional Building Pressure Control:
Address Temporal Variability & Indoor Sources

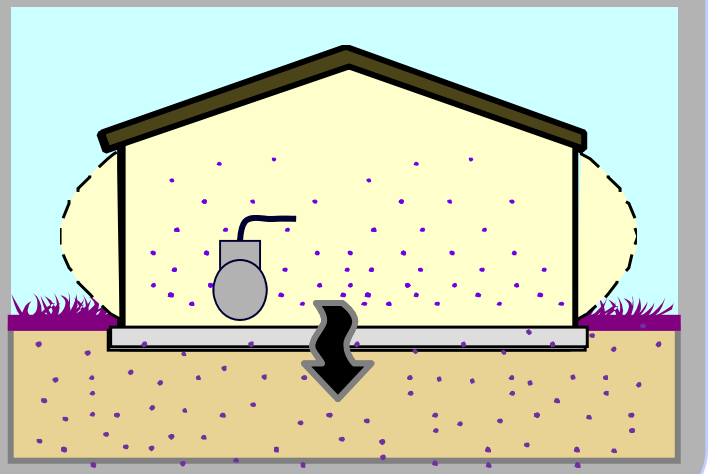
General Concept:

1) **Use controlled *NEGATIVE* pressure to *TURN ON* vapor intrusion**
2) **Evaluate potential for vapor intrusion using on-site analysis procedure**

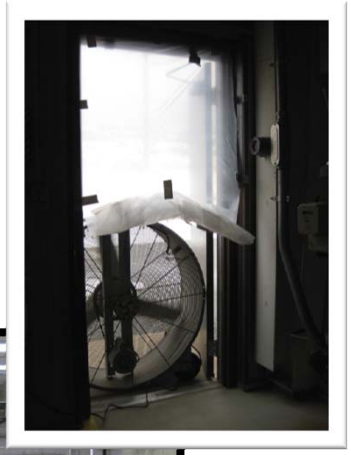
NEGATIVE
Pressure in Building = VI On



POSITIVE
Pressure in Building = VI Off



Optional Building Pressure Control: *Mixed VI and Indoor Sources*



Industrial Building Housing NAPL Recovery System

TCE in Indoor Air:

Baseline: 440 ug/m^3

Positive Pressure: 38 ug/m^3

Negative Pressure: 404 ug/m^3

Key Point: ***Pressure control showed that VI was primary source of TCE in indoor air.***

PRELIMINARY COST ASSESSMENT

COST OF VI INVESTIGATION (PER SMALL BUILDING)

On-site Analysis Method

- 1/2 – day with HAPSITE (10-20 analyses)
- 2 Confirmation Summa Samples
- Planning, reporting, etc.
- Cost = $7,900/building

Traditional Method

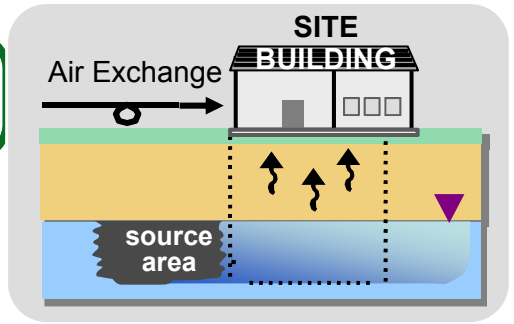
- Summa samples: 3 indoor, 1 outdoor, 3 sub-slab
- Planning, reporting, etc.
- Cost = $6,900/building

Key Point: *Costs are similar. Results from on-site analysis expected to be more definitive.*

Both cost estimates assume local consultant, multiple buildings included in investigation

Vapor Intrusion: Field Methods

- **Significance of Background Sources**
- **Stable Isotope Analysis**
- ***On-Site GC/MS Analysis***
  - ***Overview***
  - ***Investigation Protocol***
  - ***Data Quality Considerations***



DATA QUALITY CONSIDERATIONS

Data Quality Procedures

- **5-points calibration: daily to weekly**
- **Calibration checks: 2x per day**
- **Field duplicates**
- **Instrument blanks**

Data Quality Objectives

DQO	Goal	Typical
Accuracy	RPD <100%	RPD < 67%
Precision	RPD < 30%	RDP < 10%
Sensitivity	<5 ug/m^3	0.5 to 1 ug/m^3

Key Point: ***DQOs are not the same as fixed lab, but data quality is known and documented***

Wrap-Up: VI Investigations

- ***Multiple Sources:*** **VI investigations are challenging due to numerous potential sources of indoor air impacts.**
- ***Problems with Conventional Approach:*** **Use of limited measurements can lead to false conclusions re: vapor intrusion.**
- ***Advanced Methods:*** **On-site analyses and other advanced methods can identify source of VOCs in quickly (< 1 day) and economically.**